Enhanced polarization in strained BaTiO$_3$ from first principles

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ABSTRACT

The structure, polarization, and zone-center phonons of bulk tetragonal BaTiO$_3$ under compressive epitaxial stress are calculated using density functional theory within the local density approximation. The polarization, computed using the Berry-phase formalism, increases with increasing tetragonality and is found to be enhanced by nearly 70% for the largest compressive misfit strain considered (-2.28%). The results are expected to be useful for the analysis of coherent epitaxial BaTiO$_3$ thin films and heterostructures grown on perovskite substrates having a smaller lattice constant, such as SrTiO$_3$.

INTRODUCTION

With recent advances in oxide epitaxy, coherent growth of nearly perfect ultrathin perovskite films and heterostructures is now possible [1, 2, 3]. In these systems, individual constituent layers are under mixed mechanical boundary conditions: constrained to the substrate lattice constant in-plane, the films are free to relax in the normal direction. The strains achieved in this way can be quite significant, and can be controlled to tune structure, ferroelectric, and dielectric properties of these nanostructured materials [4, 5]. For example, the polarization could be increased over that of known bulk compounds [6, 7], improving the performance of ferroelectric field-effect transistors and nonvolatile memories.

When the interfaces in lattice-matched heterostructures are between sufficiently similar materials, even the thinnest layers can be well described by considering the behavior of the bulk under the same boundary conditions. Thus, for example, many properties of BaTiO$_3$/SrTiO$_3$ superlattices can be understood by considering the effects of large strains on bulk BaTiO$_3$. This has led to great interest in information about highly strained bulk and film states in the perovskites, for example as presented previously in a phenomenological Landau-Devonshire framework [7, 8, 9].

Here we perform first-principles calculations and obtain information about the structure, spontaneous polarization, and zone-center phonons of bulk tetragonal BaTiO$_3$ with misfit strains down to about -2.3%. While our results correspond to zero temperature, previous work [7] suggests that in this high-strain regime, the tetragonal phase is stable with increasing temperature and thus our analysis is relevant to the study of ultrathin BaTiO$_3$ films and BaTiO$_3$/SrTiO$_3$ superlattices at room temperature [10].

METHODOLOGY

To predict the ground state structure of strained BaTiO$_3$ and compute the associated polarization, we use density functional theory (DFT) [11] within the local density approxima-

tion (LDA) [12], as implemented with a plane-wave basis in the Vienna *ab initio* Simulations Package (VASP) [13]. Results are obtained using projector-augmented wave (PAW) [14] potentials provided with VASP. The PAW potentials explicitly treat 10 valence electrons for Sr ($4s^2 4p^6 5s^2$), 12 for Ti ($3s^2 3p^6 3d^2 4s^2$), and 6 for oxygen ($2s^2 2p^6$). The ions are steadily relaxed toward equilibrium until the Hellmann-Feynman forces are less than 10^{-3} eV/Å. Brillouin zone integrations are performed with a Gaussian broadening of 0.1 eV during all relaxations. All calculations are performed with a 6×6×6 Monkhorst-Pack **k**-point mesh and a 50 Ry plane-wave cutoff. Once ground-state structures are obtained, polarizations are determined from first principles using the Berry-phase formalism [15]. The force-constant matrices are then obtained with a frozen-phonon approach. Specifically, a series of calculations is performed in which each ion in turn is displaced along $\hat{z}$ by 0.1% of the lattice parameter and the Hellmann-Feynman forces on all the atoms computed; the phonon frequencies and eigenvectors are then acquired through diagonalization of the corresponding dynamical matrix.

RESULTS

We begin by calculating the equilibrium structural parameters of BaTiO$_3$ under zero stress. The observed phases of bulk BaTiO$_3$ are closely related to the cubic perovskite structure $Pm\bar{3}m$ [16], which is the structure of the high-temperature phase (T>403 K). The simple cubic unit cell of this structure can be chosen so the Ti cation occupies the body-centered site 1b ($\frac{1}{2}$,$\frac{1}{2}$,$\frac{1}{2}$) and is octahedrally coordinated by oxygen anions at 3c ($\frac{1}{2}$,0,$\frac{1}{2}$); the Ba cation is then at Wyckoff position 1a (0,0,0), and twelve-fold coordinated by oxygens.

The rhombohedral $P3m1$ phase is computed to be the ground state of BaTiO$_3$, consistent with observations [16]; however, it is just slightly lower in energy (only ∼1 meV per unit cell) than the optimized tetragonal $P4mm$ structure [17], the observed room temperature phase [16]. In the tetragonal phase, the simple cubic lattice distorts, resulting in two independent lattice parameters a (in-plane) and c (normal). The lower symmetry also permits relative displacement of the atomic sublattices along $\hat{z}$, with Wyckoff positions 1a (0,0,0) for Ba and 1b ($\frac{1}{2}$,$\frac{1}{2}$,$\frac{1}{2}$+Δ_{Ti}) for Ti, while two Wyckoff positions are occupied by oxygens, designated O$_\text{I}$, and O$_\text{II}$: 1b ($\frac{1}{2}$,$\frac{1}{2}$,$\Delta_{\text{O}_\text{I}}$) and 2c ($\frac{1}{2}$,0,$\frac{1}{2}$+$\Delta_{\text{O}_\text{II}}$). These displacements result in a nonzero polarization along [001].

The computed values of the structural parameters are given in the first line of Table I. Our calculated lattice parameters a=3.945 Å and c=3.988 Å are slightly smaller than those found experimentally (a=3.994 Å and c=4.036 Å [19]), the size of the underestimate being typical of that found in LDA studies of a wide variety of insulators and semiconductors. The smaller volume is known, however, to suppress the polar instability [18], and indeed the computed displacements (in reduced units of c) of 0.0122, -0.0192, and -0.0124 for Δ_{Ti}, $\Delta_{\text{O}_\text{I}}$, and $\Delta_{\text{O}_\text{II}}$, respectively, are smaller than the measured values [19], which are 0.015, -0.023, and -0.014. The polarization of the optimized tetragonal phase (P_0=24.97 μC/cm^2) is thus also significantly less than that computed with the experimental structural parameters (32.2 μC/cm^2). As a consequence, in the following we define misfit strains to be relative to the calculated lattice constants, and define polarization enhancement relative to the computed zero-stress polarization P_0.

In coherent epitaxial thin films and [001] superlattice heterostructures, the two lattice vectors in the plane of the interface are constrained to match the substrate while the third lattice vector is free to relax. Here, we consider tetragonal $BaTiO_3$ ($P4mm$) under mechanical boundary conditions corresponding to coherent epitaxy of a c-axis oriented phase on simple cubic substrates, such as $SrTiO_3$, having lattice constants slightly smaller than that of stress-free bulk tetragonal $BaTiO_3$. We perform a series of constrained relaxations in which the in-plane lattice constant a of bulk tetragonal $BaTiO_3$ is compressed (e.g., to the value of a hypothetical substrate) and the length of the normal axis and atomic positions are optimized. We consider misfit strains ranging from -0.28% to -2.28%. The absolute stabilities of the resulting structures require independent investigation. For example, it may be energetically favorable for the polarization vector and c-axis to tilt toward the [110] direction (this has been referred to as the r phase in previous work [7]), lowering the point symmetry to monoclinic. We have, however, verified that for misfit strains of -0.76% and larger, lowering the symmetry to monoclinic does not result in a lower energy, and we can therefore tentatively conclude that the $P4mm$ structure is relevant under the boundary conditions considered in this work.

The optimized structural parameters of strained c-phase $BaTiO_3$ are summarized in Table I. A tendency to conserve volume is manifested as an increase in c with increasing magnitude of the misfit strain, through this increase does not result in a full compensation of the in-plane compression and the volume actually decreases moderately. The atomic displacements relative to the centrosymmetrically-strained cubic perovskite structure exhibit a significant, nearly linear, increase with increasing misfit strain. Both the average and deviation (or splitting) of the two $Ti-O_I$ distances (along the $\hat{z}$-oriented Ti-O chain) increase with misfit strain, from 1.994 ± 0.125 Å at zero misfit to 2.066 ± 0.233 Å at -2.28%. Thus, the smaller $Ti-O_I$ distance actually decreases slightly, from 1.87 to 1.83 Å, while the larger distance increases by 8% over the same range. The shortest $Ba-O_{II}$ distance also declines modestly from 2.77 to 2.75 Å. The shortest $Ba-O_I$ distance, however, decreases more rapidly with increasing strain and, for the largest strain considered (2.28%), this separation is smaller than the minimum $Ba-O_{II}$ contact.

These structural trends are accompanied by a significant change in polarization P_s. Specifically, the increased atomic displacements associated with the increase of tetragonality (c/a) tend to increase the polarization; for 2.28% strain, the polarization *increases* by nearly a factor of two. These results are consistent with a previous first-principles study, in which a strong dependence of the polarization on the c parameter was observed for $BaTiO_3$ [6]. We also report the increase in energy per unit cell, ΔE, which reflects the energy cost of nonzero misfit strain. It varies quadratically with misfit strain over the range shown, with an estimated effective elastic constant of 135 eV/unit cell.

The computed frequencies for the $\hat{z}$ polarized zone-center phonons for each optimized structure are given in Table II. As there are five atoms in each primitive cell, 12 zone-center optical phonons are expected (plus three acoustic modes). At the zone center these are labeled by the irreducible representations of the C_{4v} point group. There are 4 A_1 modes (Raman and IR-active), 1 B_1 mode (Raman active), and 5 doubly-degenerate E modes (Raman and IR-active), of which the A_1 and B_1 modes have atomic displacements and polarization (if nonzero) only along $\hat{z}$. The frequencies of the three A_1 modes are 503, 252, and 178 cm^{-1}, respectively. These agree quite well with a room-temperature experiment,

Table I: Structural parameters of BaTiO$_3$ under in-plane compression, computed from first principles. The misfit strain (%) is measured relative to the calculated lattice parameter of the computed tetragonal phase, reported in the table as 0.0% strain. Displacements are given relative to the centrosymmetrically-strained cubic-perovskite structure with the Ba position fixed at (0,0,0) in reduced coordinates (units of c). P$_s$ is the Berry-phase polarization in μC/cm^2, with P$_0$ being the polarization of the equilibrium tetragonal structure. ΔE is the increase in energy in meV per unit cell relative to the equilibrium tetragonal structure.

%	a (Å)	c (Å)	c/a	V (Å^3)	Δ_{Ti}	$\Delta_{\text{O}_\text{I}}$	$\Delta_{\text{O}_\text{II}}$	P$_s$	P$_s$/P$_0$	ΔE
0.0	3.945	3.988	1.0110	62.06	0.0122	-0.0192	-0.0124	24.97	1	0.0
-0.28	3.934	4.0097	1.0192	62.06	0.0134	-0.0227	-0.0143	28.08	1.13	1.08
-0.76	3.915	4.0353	1.0309	61.83	0.0148	-0.0256	-0.0165	31.36	1.26	8.48
-1.26	3.895	4.0647	1.0437	61.66	0.0160	-0.0295	-0.0191	34.87	1.40	22.67
-1.77	3.875	4.0961	1.0571	61.51	0.0170	-0.0336	-0.0220	38.37	1.54	43.63
-2.28	3.855	4.1322	1.0719	61.42	0.0179	-0.0384	-0.0253	42.12	1.69	71.26

Table II: Computed zone-center phonon frequencies of BaTiO$_3$ as a function of misfit strain (%) for $\hat{z}$-polarized phonons labelled by irreducible representations A$_1$ and B$_1$.

%	ω_{A_1} (cm^{-1})			ω_{B_1} (cm^{-1})
0.0	503	252	178	294
-0.28	508	275	179	292
-0.76	514	296	180	290
-1.26	524	316	180	286
-1.77	536	332	180	282
-2.28	549	347	180	278

which reports 512, 276, and 178 cm^{-1} for the same TO modes [20]. An analysis of the corresponding eigenvectors indicates that the two highest-frequency modes involves primarily Ti and O motion; in the lowest the cations move opposite to the anions, with each ion in the primitive cell participating almost equally. The B$_1$ mode, for which the computed frequency is 294 cm^{-1}, is Raman active and involves alternating motion of the two O$_{\text{II}}$ ions. As for the A$_1$ modes, our computed frequency agrees well with the value of 308 cm^{-1} measured at room temperature [20]. We are presently unaware of previous first-principles calculations of zone-center phonon frequencies in tetragonal BaTiO$_3$, although we note previous calculations have been performed using an empirical rigid-ion model [21] and shell-model potentials [22].

In the remainder of Table II, we report the effect of in-plane compression on the frequencies of these four modes. We find that the two highest A$_1$ modes *increase* with increasing misfit strain, while the frequency of the lowest-lying A$_1$ mode is nearly independent of misfit strain down to about -2.3%. In contrast, the computed Raman-active B$_1$ mode frequency is found to *decrease* with increasing misfit strain.

DISCUSSION

The trends witnessed here in the computed properties of strained $BaTiO_3$ are quite general and reflect the underlying physics of ferroelectric perovskites under the mixed-mechanical boundary conditions associated with epitaxy. In-plane compression resulting from epitaxial stress favors expansion of c normal to the substrate and, by a mechanism analogous to that responsible for the enhancement of the ferroelectric instability with increasing volume, the polar distortion and associated polarization along $\hat{z}$ is expected to increase, as observed.

While larger polarization enhancements may in principle be achieved through larger misfit strains, the role of misfit strain in materials design is limited by a rapidly increasing strain energy ΔE. Above a critical thickness, misfit dislocations will become energetically favorable, and the film or heterostructure will relax to its bulk lattice constant, relieving stress and decreasing the polarization. However, coherent epitaxy of $BaTiO_3$-based heterostructures of useful thicknesses has already been demonstrated [2, 5], and the present results show that the misfit strain of $BaTiO_3$ on a $SrTiO_3$ substrate ($\sim$2%) is large enough to achieve significant enhancement of the polarization.

Our computed phonon frequencies are of interest chiefly for two reasons. First, combined with the computed Born effective charges and electronic dielectric constant (to be reported in a separate publication), they determine the phonon contribution to the static dielectric response ϵ_0. While clearly an important property in itself, ϵ_0 should also be relevant for understanding the effects of changing electrical boundary conditions on films and superlattices. Second, the sensitivity to strain of the mode frequencies, particularly the intermediate frequency A_1 mode, can provide an experimental probe of the strain state of a $BaTiO_3$ layer. Indeed, for the closely related material $PbTiO_3$, mode hardening has been observed in films under compressive epitaxial stress [23].

Although our focus here centers on the effects of strain, macroscopic electric fields, interfacial effects, and finite size effects must also play a fundamental role in determining the properties of coherent epitaxial thin films and superlattices. However, knowledge of strain effects has already proved to be invaluable for analyzing experimental and first-principles results [10], and for separating out the contributions of other intrinsic as well as extrinsic effects. Therefore, a broader study of $BaTiO_3$, which includes calculation of the dielectric tensor and related quantities, is currently in progress. A similar study of other perovskites, such as $PbTiO_3$, $PbZrO_3$, $SrTiO_3$, $KNbO_3$ and $KTaO_3$, would also be pertinent.

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